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THE OLD AND THE NEW KINETIC THEORY.

The Kinetic Theory of Gases. By Dr. Oskar Emil Meyer. Translated from the Second Revised Edition by Robert E. Baynes, M.A. Pp. xvi + 472. (London: Longmans, Green and Co., 1899.)

A Treatise on the Kinetic Theory of Gases. By S. H. Burbury, M.A., F.R.S. Pp. vi + 158. (Cambridge: At the University Press, 1899.)

IT is difficult for a reader at the present time to imagine himself back in the seventies before the first edition of Meyer's "Kinetische Gastheorie" appeared. After the outlines of the kinetic theory of gases had been sketched out by Clausius and Maxwell, much was needed to bring the theory into closer accord with the requirements alike of the mathematician and of the experimentalist. The back numbers of the *Wiener Sitzungsberichte* testify to the keen interest taken in the subject at the period to which we are alluding, and in connection with diffusion and other allied phenomena mainly depending on the free paths of the molecules of gases, a prominent place must be given to the writings of Oskar Emil Meyer. It was Meyer, for example, who taught us that in the diffusion of two gases whose molecules have unequal powers of penetrating into one another, a counter-current must set in to compensate for the differences of pressure which would otherwise be produced by the transference of molecules in the direction of the more penetrable gas—a theory which has met with wide acceptance.

Mr. Baynes, in preparing the English version of a new edition of Meyer's treatise, has given English readers a book calculated to meet the wants of a large and varied class of persons interested in the kinetic theory. Mathematicians will naturally turn their attention to the 112 pages of "Mathematical Appendices," and will there obtain an introduction to theories for the further development of which they will probably pass on to the writings of Boltzmann, Tait, Watson, Natanson and others; while the removal of this mathematical matter to a separate section renders the book specially suited to students of physics and chemistry who are interested with experimental conclusions rather than with abstract reasoning. It was for such readers that Meyer's first edition was written in 1877, and there can be no doubt that the book, presenting, as it does, the subject in the aspect of a physical reality and not as a mere collection of formulæ which may or may not accord with results of experiments, has done much to popularise the kinetic theory of gases, and thus indirectly to help to make its name at least familiar even to elementary pass-degree candidates. Now that we have an English edition students can have no excuse for not carrying their knowledge of the subject rather further; for a better introductory treatise could hardly be written, and there is little in Meyer's treatment that could present difficulties even to the veriest beginner. After an introductory chapter on the foundations of the theory, the relations between pressure and energy are dealt with very fully. "Maxwell's Law" is illustrated by a curve showing the distribution of speed, a diagram showing shots on a target distributed according to the error-law, and a statistical table showing the relative proportions of molecules whose speeds lie between different limits, reminding one of the statistical reports required by the Civil Service examiners. The two last illustrations well exhibit the fact that the probability of a molecule having its *speed* zero is infinitely small, and that there is a certain speed whose frequency is a maximum, notwithstanding that the most probable value of the *velocity component* in any direction is zero. In the chapter on "Ideal and actual gases," we have an account of Van der Waals' and allied hypotheses; while under the heading "Molecular and atomic energy" the specific heat ratios of gases and their dependence on the number of degrees of freedom of a molecule for heat-motions are discussed.

The second part deals with molecular free paths and the phenomena depending on them. It contains an exhaustive account of all that has been done in explaining viscosity, diffusion, and heat-conduction by the kinetic theory, the part on viscosity alone extending over seventy-six pages. The third part, which is much shorter than the two preceding ones, deals with "direct properties of molecules," including determinations of the size, number, and speed of molecules and the magnitudes of intermolecular forces. This concludes the physical portion of the book. In the mathematical appendices, the calculations are in many cases based both on Clausius' hypothesis of equal speeds, and also on Maxwell's distribution, and while the former method is at the present day of purely academic interest, its inclusion may be serviceable to beginners. Mr. Baynes has supplied an index besides adding to the already copious references to original memoirs, which are an important feature of the treatise. While a number of new theories have been inserted, and on the other hand many recent developments have been excluded, the author has perhaps wisely made the general scope and plan of the book the same as in the first edition. As he remarks in his preface,

"with the present limitation to the old range it has cost very much trouble and very much time to work up the literature of the subject, which has grown mightily in these more than twenty years."

While Prof. Meyer and Mr. Baynes are contented to accept "Maxwell's Law" as a working hypothesis, Mr. Burbury has taken up the far more difficult task of working out the distribution of a system of molecules under conditions to which the ordinary proofs of the Boltzmann-Maxwell distribution are inapplicable, viz. when finite intermolecular forces exist, or when the volume of the molecules is not infinitely small compared with the total volume of the gas. The appearance during recent years of several papers from Mr. Burbury's pen has acquainted us with the general character of his labours, which involve practically the foundation of a new kinetic theory, and we are glad to read the general conclusions in the form of a handy treatise. In investigating the distribution of molecular co-ordinates and momenta, Burbury points out that we may take two different fundamental assumptions for our starting-point, namely, "Condition A," that the chance of any molecule having velocity components within given limits *is* independent of the

distribution of co-ordinates and velocities of the other molecules; or "Condition B," that the chance of a given molecule having at any instant assigned velocities *is not* independent of the positions and velocities of all the other molecules at the instant. Condition A readily leads to the Boltzmann-Maxwell distribution, but Burbury finds that the assumption of Condition B (which is, of course, of wider application than Condition A) leads to a new law of distribution, according to which the chance of a system of molecules having their velocity components within the limits of the multiple differential of these components is

$$Ce^{-hQ}du_1dv_1dw_1 \ . \ . \ . \ du_ndv_ndw_n,$$

where

$$Q = \Sigma m(u_r^2 + v_r^2 + w_r^2) + \Sigma\Sigma b_{rs}(u_ru_s + v_rv_s + w_rw_s).$$

The b coefficients are functions of the distance between the molecules, which become inappreciable except when this distance is very small. When the b coefficients are negative, their meaning is that two near molecules are more likely to be moving in the same than in opposite directions, and the motions of the molecules are then said to be *correlated;* while in the opposite case of b_{rs} positive the motions are said to be *contrarelated.* It should be observed that $u_ru_s + v_rv_s + w_rw_s$ is equal to q_rq_s cos e where $q_r q_s$ are the speeds, e the angle between their directions.

The view that the ultimate distribution differs from the Boltzmann-Maxwell distribution being at variance with the results of "Boltzmann's Minimum Theorem," Burbury carefully examines the proof given by Boltzmann, and concludes that "what the H theorem proves then is this, that the distribution of velocities expressed by the equation $F'f' = Ff$ is the only distribution which can be permanent consistent with the existence, and the continued existence of Condition A or its equivalent." In the motion obtained by reversing the velocities Condition A is not satisfied. Burbury considers that in this proof Boltzmann's assumption that the motion is "molecular ungeordnet" is equivalent to "Condition A." He remarks:—

"Let us endeavour to construct synthetically a system which shall without doubt be molecular ungeordnet. The molecules being distinguished by numbers, I ask (say) Dr. Watson to assign velocities to them according to any law he pleases. Then I, in complete ignorance of those assigned velocities, scatter the molecules at haphazard through space, and they shall start from the positions which I so give them with the velocities so assigned them by Dr. Watson. That is *primâ facie* a molecular ungeordnet system; in fact, it is as near an approach to chaos as is possible in an imperfect world."

Burbury next proves that if the intermolecular forces, are finite, Condition A cannot exist, and $uu' + vv' + ww$ has an average finite value, a function of r which is positive if the forces are repulsive. This proof involves the assumption that $\overline{uu'}$ is zero in the absence of intermolecular forces, and we are told:

"Strictly, n the number of molecules in the system being finite and the centre of inertia at rest, it must be negative, but it may be neglected when n is great."

This is rather a difficult assumption to accept without further explanation. The proof that "correlation" must exist when the molecules are equal elastic spheres is much more laborious. In the chapter on "General theory of the stationary motion," it is shown that "Maxwell's law of partition of energy" does not necessarily hold except when Condition A is satisfied. This is as it should be; otherwise the heat given to a polyatomic gas would be divided equally between all the atoms of all the molecules, instead of being divided, as Boltzmann teaches us, mainly between the translatory and rotatory motions of the molecules, which are the only motions to which Condition A is applicable.

Under the title "On molecules as carriers," we have a short account of Boltzmann's simple method of treating diffusion and allied phenomena, based on the latter's "Vorlesungen über Gastheorie." We hope that the general mathematical reasoning on which Burbury's theory of correlation rests is not to be gauged by his method of investigating the mean free path on p. 115, in which he says: "Let $1 - \pi c^2 N\lambda/\omega = \phi(\lambda) = \phi$," and a few lines later infers that $\phi = e^{-k\lambda}$ where $k = \pi c^2 N/\omega$, and $k\lambda$ is finite.

The chapter on "Thermodynamical relations" well brings out the fact that while Burbury's new distribution, like the conventional one, fulfills the condition that dQ has an integrating divisor, the usual symbol for which (in this country) is the first letter of the word "Temperature," but little progress has so far been made in explaining the fundamental properties of temperature by molecular motions. The properties of irreversible thermodynamics are nowhere more manifest than in the friction, heat conduction, and imperfect elasticity of solid bodies whose molecules are not only correlated, but appear inseparably interlocked. Yet hardly any headway has been made in getting the equation of energy-equilibrium between two bodies into a form analogous to that expressing equality of temperature, except under highly specialised assumptions as to the law of distribution of energy, which prevent the conclusions from being applied to any but attenuated gases. Every attempt to advance in the desired direction has hitherto led to hopeless mathematical difficulties.

A discussion on the merits of Burbury's new method of analysis would be out of place in the present review. His theory represents the outcome of much thinking, and is not to be disposed of hastily. It boldly faces the question of correlation, and thus brings us one step nearer towards explaining the properties of dense assemblages of molecules. It has the remarkable property that the character of the motion changes completely when the expression Q ceases to be essentially positive, by the vanishing of the determinant of the coefficients of Q or of one of its leading minors; and we know that the state of a gas also suddenly changes by liquefaction. Seeing, however, that it is necessary to regard actual molecules, not as spheres or material points, but rather as non-spherical rigid bodies, it still remains for Burbury to tackle the far more difficult question of the distribution of translatory and rotatory motions of unsymmetrical or axially symmetrical molecules when correlation exists. And we have a kind of vague feeling that probability considerations and finite molecular forces which are functions of the distances and positions of the molecules are bringing us not much nearer the desired goal of explaining temperature. Indeed, the question of deducing the

laws of irreversible heat-phenomena from probability considerations becomes more and more difficult the more it is studied. But physicists have given us another source of irreversibility, of which the kinetic theorist has hitherto made little use. The equation

$$\frac{d^2(r\phi)}{dt^2}=a^2\frac{d^2(r\phi)}{dr^2}$$

representing propagation of spherical waves is satisfied mathematically by $r\phi=F(at+r)+f(at-r)$; but the physicist has to make the axiom that waves always radiate *from*, and never converge *to* a source of disturbance, and hence, that the second term alone exists in nature. Seeing that the molecules on our earth derive so much of their heat-energy from the sun, which energy is (if we may use the expression) transported across some ninety million miles of ether by equations of this type, it is surely desirable that some working hypothesis should be formulated for the conversion of radiant energy into energy of heat motion, and a kinetic theory involving such a hypothesis would explain irreversibility as a natural consequence of the simple axiom involved in the suppression of $F(at+r)$.

We trust that neither Mr. Burbury nor Prof. Boltzmann will construe any of these remarks into expressions of criticism on the points of difference between their conclusions, and we hope that ere long both these writers will enlighten us further on the questions at issue. The writer of the present review has (doubtless in common with many others) spent a considerable amount of time in trying to attack that tantalising question of temperature from a kinetic standpoint coupled with probability considerations, or even deducing the law of molecular distribution from the temperature-property; but every attempt leads to an impenetrable wall built of dense assemblages of molecules which cannot be assumed to follow the Boltzmann-Maxwell distribution, and which seem to say to the mathematician, "Thus far shalt thou go, but no further." G. H. BRYAN.

THE ZOOLOGY OF THE INDIAN SEAS.

A Descriptive Catalogue of the Indian Deep-Sea Fishes in the Indian Museum. Pp. iii+212 and viii.

An Account of the Deep-Sea Brachyura. Being Systematic Reports upon the Materials collected by the Royal Indian Marine Survey Ship "Investigator," 1874–1899. By A. Alcock, M.B. Pp. ii+85. (Calcutta: Printed by the Trustees of the Indian Museum, 1899.)

THE Catalogue of Deep-Sea Fishes is a monumental work, since it completes the description in full of a large number of species already listed in the author's papers, now well known, and illustrated in the "Illustrations of the Zoology of the *Investigator*" which he inaugurated in 1892, and which, thanks to the skill of his native artists, is likely to become classic.

The fishes dealt with number 169 species, the Anacanthini and Physostomi being, as might be expected, in the majority, and but two of them Plectognathi. 126 of these stand to the record of the *Investigator* alone, and 43 only appear identical with species found elsewhere; 23 are said to be common to the Indian seas and the Atlantic, and a special feature is the occurrence of a Trachinoid fish (*a Bembrops*) originally found in Japan. Dr. Gunther, as is pointed out, has already familiarised us with the idea of a former open connection between the Mediterranean and Japanese seas; and, discussing this fish and certain related forms, the author dismissing the "comfortable formula" "similarity of conditions," is led to the conclusion that "a considerable part of the fish-fauna of the Oriental region originated from, and to a certain extent is a remnant of, the fauna of the Tertiary Mediterranean of Suess—of a Mediterranean that extended from the present Gulf of Mexico, through the present Mediterranean basin, far into the eastern hemisphere."

The chief novelty of the present work is a chart compiled from Koken's "Vorwelt und ihre Entwickelungsgeschichte" with the object of rendering clear the bearings of the above conclusion. The present coast-lines and those supposed to have existed during the Tertiary period are indicated in dissimilar contours, and the presumed area of the Inland Sea is rendered appropriately clear. In the construction of this chart the author has sought the advice by Mr. T. H. Holland, formerly of the Royal College of Science, London, and that gentleman's splendid work on the Geological Survey of India amply justifies the choice.

The fresh-water fishes (mainly Ostariophyseæ and Cichlidæ) come in for consideration. The occurrence of a Symbranchid species common in Tropical America and Australia, of Cyprinodonts known from Tropical Africa and America, are duly emphasised, while the author's records concerning the Cichlidæ (Chromides) have an especial value now that our knowledge of this remarkable group is being revolutionised by our distinguished English Ichthyologist, Boulenger.

It is praise sufficient to remark that this grand monograph in no way falls short of its predecessors we have so recently reviewed (see NATURE, vol. lx. p. 459), and that it will remain for generations a standard work of reference.

The report on the Brachyura is serial with those on the Madreporaria and Ophiuroidea, and, like the former, is prefaced by an account of the history of the expedition and of its association with the Indian Museum. It completes the work of the expedition on the crabs, and as regarding descriptions of new species it is supplemental to a series of earlier papers by the author, his former associate and predecessor in office, the late Prof. Wood-Mason, and his present colleague, Dr. A. R. L. Anderson, extending over a period of more than twenty years. The present volume deals with 53 species and 38 genera, with two exceptions from depths of over 100 fathoms; and of these 21 genera and 5 species are known from other seas. Interest centres in the discovery of affinities between the fauna of the Indian and Atlantic deep-sea areas, which the author is disposed to interpret as indicative of a former open connection between the two, for which he has already argued in reporting upon the Madreporaria. Bathymetrically one species only (an *Ethusa*) was obtained at a depth exceeding 1000 fathoms, 3 (*Ethusa*, 2 sp. and a *Hypsophrys*) between 800 and 1000 fathoms, 3 between 500 and 800, and 18 between 400 and 500, while of the majority obtained at depths of from 100 to 400 fathoms